On the Quantum Theory of the Simple Zeeman Effect.

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§ 1.

The aim of this paper is to put forward a theory of the simple Zeeman effect which possesses the same general features as those of the corresponding theory in the case of the Stark effect already developed by Epstein and Schwarzschild. These general features may be briefly described as follows:—(1) The steady states of the atom are governed by classical dynamics subject to certain conditions, the quantum restrictions, which define the atom *both in the absence and in the presence of the field*; (2) radiation occurs during the period of transition from one steady state to another according to Bohr's energy relation $h\nu = W_m - W_n$.

The essential difference between our treatment and the already existing Bohr-Sommerfeld theory* lies in this: That the relation between the motion of the atom, in the presence and in the absence of the magnetic field respectively, as defined by classical dynamics, is not assumed in the former, whereas it plays a fundamental *rôle* in the latter. This relation (which we shall refer to as Schott's theorem)† involves for its classical proof a consideration of the motion of the atom during the period of establishment of the magnetic field. But the atomic system during that period is not a conservative one, and hence cannot be claimed to be fully comprehended from the point of view of the quantum theory. Thus it would seem desirable to avoid assuming Schott's theorem in a quantum treatment of the Zeeman effect. Our treatment, in which such an assumption is avoided, is, however, not incompatible with that theorem; in fact, it could be proved‡ that the latter follows as a necessary consequence of our analysis.

With regard to the quantum restrictions which define the steady states, we find it necessary to employ not the original form proposed for them by Dr. Wilson,§ but a slightly extended form first suggested by Prof. Wilson himself in the course of a discussion on the quantum theory at the Edinburgh meeting of the British Association last summer (1921). This latter form,

* See, *e.g.*, A. Sommerfeld, 'Atombau und Spectrallinien,' 2 Auf., 6 Kap., § 5, Braunschweig, 1921.

† See G. A. Schott, 'Electromagnetic Radiation,' Cambridge University Press, § 302, p. 317 (1912).

‡ See Appendix.

§ William Wilson, 'Phil. Mag.,' vol. 29, p. 796 (1915), set of equations (2).

represented by equations (17A) below, was put forward by Prof. Wilson on perfectly general grounds and apart from a theory of any particular phenomenon. The present writer was led to a special application of the same extension, represented by equations (17B) below, from a theoretical study of the Zeeman effect.

We propose, in the first place, to show that if the original form of the quantum restrictions is maintained, *both in the presence as in the absence of the field,* then there can strictly be no difference between the energies of corresponding static paths in the two cases, and consequently no theoretical ground for the spectral resolution. Secondly, we shall show that the extended form of the restrictions leads to the simple Zeeman effect.

§ 2.

We consider the motion of an electron in the neighbourhood of a heavy nucleus and in the presence of a steady magnetic field H. If W is the sum of kinetic and potential energies we have* in spherical polars (r, θ, ψ):

$$E_{\text{kin}}+E_{\text{pot}} = m_0c^2\left(\frac{1}{\sqrt{(1-\beta^2)}}-1\right)-\frac{eE}{r} = W,$$

or

$$\frac{1}{\sqrt{(1-\beta^2)}} = 1+\frac{W+eE/r}{m_0c^2}, \tag{1}$$

where m and $(-e)$ are the "proper mass" and charge of the electron respectively, E the charge on the nucleus, c the velocity of light, and $c\beta$ the velocity of the electron. Also

$$\beta^2 = \frac{1}{c^2}(\dot{r}^2+r^2\dot{\theta}_2+r^2\sin^2\theta\,\dot{\psi}^2) = \frac{1}{c^2m^2}(p_r{}^2+\frac{1}{r^2}p_\theta{}^2+\frac{1}{r^2\sin^2\theta}p_\psi{}^2),$$

where

$$p_r = m\dot{r}, \quad p_\theta = mr^2\dot{\theta}, \quad p_\psi = mr^2\sin^2\theta\dot{\psi}, \tag{2}$$

are the generalised momenta, m being the mass (variable) of the electron, so that

$$m = m_0/\sqrt{(1-\beta^2)}. \tag{3}$$

We thus have, using (2) and (3),

$$\frac{1}{1-\beta^2} = 1+\frac{1}{c^2m^2{}_0}(p_r{}^2+\frac{1}{r^2}p_\theta{}^2+\frac{1}{r^2\sin^2\theta}p_\psi{}^2). \tag{4}$$

And from (1) and (4)

$$p_r{}^2+\frac{1}{r^2}p_\theta{}^2+\frac{1}{r^2\sin^2\theta}p_\psi{}^2 = 2m_0W+\frac{2m_0eE}{r}+\frac{1}{c^2}\left(W+\frac{eE}{r}\right)^2, \tag{5}$$

* Neglecting the ratio of m_0 to the mass of the nucleus.

which defines the total energy of the motion in terms of the Hamiltonian co-ordinates. Now*

$$\frac{d}{dt}(p_i - e\alpha_i) + \partial \mathrm{W}/\partial q_i = -e \sum_s \frac{\partial \alpha_s}{\partial q_i}\frac{dq_s}{dt}, \tag{6}$$

where α is the generalised magnetic vector potential given by

$$\partial \alpha_3/\partial q_2 - \partial \alpha_2/\partial q_3 = g_2 g_3\, \mathrm{H}_1/c, \text{ and two similar equations,} \tag{7}$$

$g\,dq$ being lineal. On applying (6) to the co-ordinate ψ we get

$$\frac{d}{dt}(p_\psi - e\alpha_\psi) = 0, \qquad \text{so that} \qquad p_\psi - e\alpha_\psi = \mathrm{F}, \tag{8}$$

where F is a constant. Or since

$$e\alpha_\psi = e\mathrm{H}r^2 \sin^2\theta/2c = m_0\omega r^2 \sin^2\theta, \tag{9}$$

where

$$\omega = \tfrac{1}{2} e\mathrm{H}/m_0 c, \tag{10}$$

we have from (8) and (9)

$$p_\psi = \mathrm{F} + m_0\omega r^2 \sin^2\theta. \tag{11}$$

Substituting from (11) and (5) we have

$$r^2[-p_r^2 + 2m_0\mathrm{W} + (2m_0 e\mathrm{E})/r + 1/c^2(\mathrm{W} + e\mathrm{E}/r)^2 - 2m_0\mathrm{F}\omega]$$
$$= p_\theta^2 + \mathrm{F}^2/\sin^2\theta + m_0^2\omega^2 r^4 \sin^2\theta. \tag{12}$$

And in this last equation the variables are separable if we neglect the term in ω^2: thus

$$r^2[-p_r^2 + 2m_0\mathrm{W} + (2m_0 e\mathrm{E})/r + \frac{1}{c^2}(\mathrm{W} + e\mathrm{E}/r)^2 - 2m_0\mathrm{F}\omega]$$
$$= p^{\theta 2} + \mathrm{F}^2/\sin^2\theta = p^2 \text{ (say)},\dagger \tag{13}$$

giving

$$p_r = \sqrt{(\mathrm{A} + 2\mathrm{B}/r + \mathrm{C}/r^2)}, \tag{14}$$

$$p_\theta = \sqrt{(p^2 - \mathrm{F}^2/\sin^2\theta)}, \tag{15}$$

where

$$\left.\begin{aligned} \mathrm{A} &= 2m_0\mathrm{W}(1 + \mathrm{W}/2m_0c^2 - \mathrm{F}\omega/\mathrm{W}) \\ \mathrm{B} &= e\mathrm{E}m_0(1 + \mathrm{W}/m_0c^2) \\ \mathrm{C} &= -(p^2 - e^2\mathrm{E}^2/c^2) \end{aligned}\right\}. \tag{16}$$

§ 3.

If now we assume for the quantum restrictions their older form, viz.,

$$\int_0 p_i\, dq_i = n_i h, \qquad i = 1, 2, 3 \ldots \tag{17}$$

* See G. A. Schott, *loc. cit.*, p. 292.

† As will be seen from equation (27A) below, p is the constant angular momentum in the plane of the original motion (before the field is impressed).

where the integration extends over the period of variation of q_i, we have from (11), (14), and (15):

$$\left.\begin{aligned}&\int_0 \sqrt{(\mathrm{A}+2\mathrm{B}/r+\mathrm{C}/r^2)}\,dr = n_1 h &(\alpha)\\ &\int_0 \sqrt{(p^2-\mathrm{F}^2/\sin^2\theta)}\,d\theta = n_2 h &(\beta)\\ &\int_0^{2\pi} (\mathrm{F}+m_0\omega r^2\sin^2\theta)\,d\psi = n_3 h &(\gamma)\end{aligned}\right\} \qquad (18)$$

where the integration in the first two cases extends from the minimum value to the maximum value, and back again to the minimum value of the two respective independent variables. The first equation in (18) yields, by the method of contour integration in the complex plane,*

$$2\pi i(\sqrt{\mathrm{C}}+\mathrm{B}/\sqrt{\mathrm{A}}) = n_1 h. \qquad (19)$$

(18 β) easily yields by elementary methods, on writing $x = \cos\theta$,

$$p-\mathrm{F} = n_2 h/2\pi. \qquad (20)$$

For the third integral we have to evaluate

$$\mathrm{I} = \int_0^{2\pi} m_0\omega r^2 \sin^2\theta\, d\psi = \omega\int_0^{\tau}\sqrt{(1-\beta^2)}\,p_\psi\,dt$$

by (2) above, where τ is the time during which ψ changes from 0 to 2π. On substituting for p_ψ from (11) and neglecting ω^2, we have

$$\mathrm{I} = \omega\,\mathrm{F}\int_0^{\tau}\sqrt{(1-\beta^2)}\,dt.$$

Let τ_0 be the value of τ calculated for $\omega = 1/c = 0$, *i.e.*, the value calculated in the absence of the field and without taking account of the relativity correction; we see that

$$\mathrm{I} = \omega\mathrm{F}(\tau_0 + \text{terms in } \omega \text{ and } 1/c),$$

so that, neglecting higher powers of ω than the first and products of ω and $1/c$, we have

$$\mathrm{I} = \omega\mathrm{F}\tau_0. \qquad (21)$$

Also
$$\tau_0 = \frac{\pi a_0 b_0}{\frac{1}{2}p_0/m_0}, \qquad (22)$$

$\frac{1}{2}p_0/m_0$ being the areal velocity of the electron in the elliptic path, defined in the absence of the field, whose major and minor semi-axes are a_0 and b_0 respectively; these constants could be calculated from our analysis by

* See Sommerfeld, *loc. cit.*, p. 477; our $\sqrt{\mathrm{C}}$ corresponds to his $(-\sqrt{\mathrm{C}})$.

putting $\omega = 1/c = 0$ everywhere. The values thus obtained are identical with those obtained by Sommerfeld* by simpler methods, thus:—

$$\left.\begin{aligned} a_0 &= h^2(n_1+n)^2/[(2\pi)^2 m_0 e\mathrm{E}] \\ b_0 &= [h^2 n(n+n_1)]/[(2\pi)^2 m_0 e\mathrm{E}] \\ p_0 &= nh/2\pi \end{aligned}\right\}, \tag{23}$$

where
$$n = n_2 + n_3, \tag{24}$$

so that we have finally for the third quantum restriction

$$\mathrm{F} = n_3 h(1-\kappa)/2\pi, \tag{25}$$

where
$$\kappa = [\omega h^3(n+n_1)^3]/[(2\pi)^3 m_0 e^2 \mathrm{E}^2]. \tag{26}$$

And from (20) and (25)

$$p = nh(1-\kappa n_3/n)/2\pi. \tag{27}$$

In order to calculate the energy W of the static paths, let

$$\mathrm{W} = \mathrm{W}_0 + \underset{\omega}{\delta \mathrm{W}} + \underset{c}{\delta \mathrm{W}}, \tag{28}$$

where W_0 is the value obtained for $\omega = 1/c = 0$, and $\underset{\omega}{\delta \mathrm{W}}$ and $\underset{c}{\delta \mathrm{W}}$ being first order terms in ω and $1/c^2$ respectively; and adopt a similar notation for A, B and C. We see from (16) that

$$\left.\begin{aligned} &\mathrm{A}_0 = 2m_0\mathrm{W}_0,\ \underset{\omega}{\delta \mathrm{A}} = 2m_0\left(\underset{\omega}{\delta \mathrm{W}} - \frac{n_3 h\omega}{2\pi}\right),\ \underset{c}{\delta \mathrm{A}} = 2m_0\mathrm{W}_0\left(\frac{\mathrm{W}_0}{2m_0c^2} + \frac{\underset{c}{\delta \mathrm{W}}}{\mathrm{W}_0}\right) \\ &\mathrm{B}_0 = e\mathrm{E}m_0,\quad \underset{\omega}{\delta \mathrm{B}} = 0, \qquad\qquad \underset{c}{\delta \mathrm{B}} = \frac{e\mathrm{EW}_0}{c^2} \\ &\mathrm{C}_0 = -\frac{n^2h^2}{(2\pi)^2},\ \underset{\omega}{\delta \mathrm{C}} = \frac{2h^2\kappa n n_3}{(2\pi)^2}, \qquad \underset{c}{\delta \mathrm{C}} = \frac{e^2\mathrm{E}^2}{c^2} \end{aligned}\right\} \tag{29}$$

where only first-order small terms are considered. W_0 is obtained from (19) and (27) on putting $\omega = 1/c = 0$. Thus:—

$$\mathrm{W}_0 = \frac{-\mathrm{N}h(\mathrm{E}/e)^2}{(n_1+n)^2}, \tag{30}$$

where N is the Rydberg constant:

$$\mathrm{N} = 2\pi^2 e^4 m_0/h^3. \tag{31}$$

The values of the two terms on the right-hand side of (19) may now be written to the first order, using (29):—

$$2\pi i\sqrt{\mathrm{C}} = -nh\left[1 - \frac{(2\pi)^2 e^2\mathrm{E}^2}{2n^2h^2c^2} - \frac{\kappa n_3}{n}\right]. \tag{32}$$

$$2\pi i\frac{\mathrm{B}}{\sqrt{\mathrm{A}}} = (n+n_1)h\left[1 + \frac{\mathrm{W}_0}{c^2 m_0} - \frac{1}{2\mathrm{W}_0}\left(\underset{\omega}{\delta \mathrm{W}} - \frac{n_3 h}{2\pi}\omega\right) - \tfrac{1}{2}\left(\frac{\mathrm{W}_0}{2m_0c^2} + \frac{\underset{c}{\delta \mathrm{W}}}{\mathrm{W}_0}\right)\right], \tag{33}$$

* *Loc. cit.*, p. 267. Sommerfeld's n' corresponds to our n_1.

so that we have from (19), on equating the terms in ω to zero from the two sides of the equation, using (32) and (33),

$$\underset{\omega}{\delta W} = \frac{n_3 h\omega}{2\pi} + \frac{2 W_0 \kappa n_3}{n+n_1},$$

which yields, on substituting for κ and W_0 from (26) and (30) respectively,

$$\underset{\omega}{\delta W} = 0, \qquad (34)$$

so that *the energy of any static path defined in the presence of the field by the quantum numbers n_1, n_2, n_3, would be the same as that of the corresponding path defined in the absence of the field by the same quantum numbers.* This would obviously lead to no Zeeman effect at all.

§ 4.

Instead of (17), let us now maintain the slightly extended form

$$\int_0 (p_i - e\alpha_i)\, dq_i = n_i h, \quad i = 1, 2, 3\ldots, \qquad (17\text{A})$$

where the integration extends as before over the period of variation of q_i. Proceeding in a similar manner as in § 3, and remembering that $\alpha_r = \alpha_\theta = 0$ and that α_ψ is given by (9), we now have

$$\int_0 (p_\psi - m_0\omega r^2 \sin^2\theta)\, d\psi = n_3 h, \qquad (17\text{B})$$

or

$$\int_0^{2\pi} F\, d\psi = n_3 h, \qquad (18\gamma\text{A})$$

so that F and p are now given respectively by

$$F = n_3 h/2\pi \qquad (25\text{A})$$

and

$$p = nh/2\pi, \qquad (27\text{A})$$

equations (19), (20) and (24) being still maintained. And adopting the same notation as before, we see that (29) still holds good except for the value of $\underset{\omega}{\delta C}$, which is now given by

$$\underset{\omega}{\delta C} = 0.$$

This leads, instead of (32), to the equation

$$2\pi i\sqrt{C} = -nh\left[1 - \frac{(2\pi)^2 e^2 E^2}{2n^2h^2c^2}\right], \qquad (32\text{A})$$

(30), (31) and (33) being unaffected. So that, finally, on equating the terms

in ω and $1/c^2$ respectively to zero from the two sides of (19), using (32A) and (33), we have

$$\underset{\omega}{\delta}\mathrm{W} = n_3 h\omega/2\pi, \tag{34A}$$

$$\underset{c}{\delta}\mathrm{W} = \frac{-2\mathrm{W}_0{}^2}{m_0 c^2}\left[\tfrac{1}{4}+\frac{n_1}{n}\right] = \frac{-\mathrm{N}\gamma h\,(\mathrm{E}/e)^4}{(n_1+n)^4}\left[\tfrac{1}{4}+\frac{n_1}{n}\right], \tag{35}$$

where γ is a small quantity given by

$$\gamma = 4\pi^2 e^4/c^2 h^2. \tag{36}$$

§ 5.

The application of equation (34a) to the hydrogen atom, the singly ionised helium atom, the doubly ionised lithium atom, etc., leads in each case to a change of frequency

$$\underset{\omega}{\delta}\nu = \omega\,(m_3-n_3)/2\pi, \tag{37}$$

where m refers to a path of greater energy than the n-path. And, further, on applying Bohr's correspondence principle, we have

$$m_3-n_3 = 0 \quad \text{or} \quad \pm 1, \tag{38}$$

corresponding to the p- and n-components respectively. So that

$$\left.\begin{array}{ll} \underset{\omega}{\delta}\nu = 0 & \text{for } p\text{-components} \\ \text{or } \pm e\mathrm{H}/4\pi m_0 c & \text{for } n\text{-components} \end{array}\right\}. \tag{39}$$

The formula (35) leads to the ordinary fine structure of the spectral "line" in question, and we see that the effect of the field is to split up each component of the fine structural group into a simple Zeeman triplet.

Appendix.

To show that if $\Sigma_{i,1}$, $\Sigma_{i,2}$, ... $\Sigma_{i,s}$, ..., etc., and Σ_1, Σ_2, ... Σ_s, ..., etc., are the paths defined by the extended quantum restrictions, in the absence and in the presence of the field respectively, then the relation between $\Sigma_{i,s}$ and Σ_s is what it would be on classical dynamics, if an electron moving along $\Sigma_{i,s}$ were to be made to move along Σ_s by the introduction of the magnetic field.

The equations defining any static path Σ_s are obtained from the results of § 2 of the text as follows: We have from (2), (14) and (15),

$$\left.\begin{array}{l} p_r = m\dot{r} = \sqrt{(\mathrm{A}+2\mathrm{B}/r+\mathrm{C}/r^2)} \\ p_\theta = mr^2\dot{\theta} = \sqrt{\{p^2-(\mathrm{F}^2/\sin^2\theta)\}} \end{array}\right\}. \tag{i}$$

The first of these questions gives

$$\frac{dt}{dr} = \frac{m_0}{\sqrt{(1-\beta^2)}} \times \frac{1}{\sqrt{(\mathrm{A}+2\mathrm{B}/r+\mathrm{C}/r^2)}},$$

and on substituting the value of $1/\sqrt{(1-\beta^2)}$ from equation (1) of the text and integrating, we get

$$t = \int_{r_0}^{r} \frac{m_0 + \dfrac{W+eE/r}{c^2}}{\sqrt{(A+2B/r+Cr^2)}}\, dr \tag{ii}$$

where r_0 corresponds to $t=0$.

Further, on making the substitution

$$\cos\theta = \sin\alpha\cos\phi, \tag{iii}$$

where

$$\cos\alpha = F/p, \tag{iv}$$

we have

$$\dot{\phi} = \frac{\sin\theta\,\dot{\theta}}{\sin\alpha\,\sin\phi},$$

so that

$$mr^2\dot{\phi} = \frac{mr^2\sin\theta\,\dot{\theta}}{\sqrt{(\sin^2\theta-\cos^2\alpha)}} \text{ from (iii)} \quad = p\times\frac{mr^2\,\dot{\theta}}{\sqrt{\{p^2-(F^2/\sin^2\theta)\}}} \text{ from (iv)}.$$

Or, on using the second equation of (i) we see that

$$mr^2\dot{\phi} = p,$$

which, with the first equation of (i), gives

$$r^2\frac{d\phi}{dr} = \frac{p}{\sqrt{(A+2B/r+C/r^2)}} \quad \text{or} \quad \phi = \int_{r_0}^{r}\frac{p\,dr}{r^2\sqrt{(A+2B/r+C/r^2)}}. \tag{v}$$

We also have from (2) and (11) of the text

$$p_\psi = mr^2\sin^2\theta\dot{\psi} = F + m_0\omega r^2\sin^2\theta.$$

And on eliminating r^2 between this and the second equation of (i) we get

$$\dot{\psi} - \omega\sqrt{(1-\beta^2)} = \frac{F}{\sin^2\theta\sqrt{\{p^2-(F^2/\sin^2\theta)\}}},$$

which yields on using (iv)

$$\dot{\psi} - \omega\sqrt{(1-\beta^2)} = \frac{\dot{\theta}}{\sin^2\theta\sqrt{(\tan^2\alpha-\cot^2\theta)}}.$$

If we introduce the variable time co-ordinate t' defined by

$$dt'/dt = \sqrt{(1-\beta^2)}, \tag{vi}$$

we now have

$$\frac{d\psi}{dt'} - \omega = \frac{d\theta/dt'}{\sin^2\theta\sqrt{(\tan^2\alpha-\cot^2\theta)}};$$

which gives on integration

$$\cos(\psi-\omega t'-\Delta) = \cot\alpha\,\cot\theta, \tag{vii}$$

where Δ is an arbitrary constant depending on the values of ψ and θ at $t=0$. The five equations (iii) to (vii) define the path of the electron, whilst equation (ii) defines the mode in which it is described for any given set of

values of the five constants involved, viz., W, F, p, r_0, and Δ. The equations defining the path $\Sigma_{i,s}$, in the absence of the field, are clearly obtained from the above equations defining Σ_s on putting $H = 0$ everywhere, and writing for the constants involved a corresponding set of values (denoted by the suffix i). We thus have for $\Sigma_{i,s}$

$$\left.\begin{aligned} t = \int_{r_{0,i}}^{r} \frac{m_0+W_i+eE/r}{\sqrt{(A_i+2B_i/r+C_i/r^2)}}\,dr, \quad \phi = \int_{r_{0,i}}^{r} \frac{p_i\,dr}{r^2\sqrt{(A_i+2B_i/r+C_i/r^2)}} \\ \cos(\psi-\Delta_i) = \cot\alpha_i \cot\theta \\ \text{where} \qquad \cos\theta = \sin\alpha_i\cos\phi, \qquad \cos\alpha_i = F_i/p_i. \end{aligned}\right\} \quad \text{(viii)}$$

Now the extended quantum restrictions define the relations between some of these constants according to equations (25A), (27A), and (34A), thus

$$p = p_i = nh/2\pi; \quad F = F_i = n_3h/2\pi; \quad W = W_i+\omega F_i. \qquad \text{(ix)}$$

So that, remembering the meanings of A, B, C given by equations (16) of the text and neglecting (as in the text) terms in ω/c^2, and in ω^2 and higher powers, we have on applying (ix)

$$A = A_i, \quad B = B_i, \quad C = C_i, \quad \alpha = \alpha_i, \quad \frac{W+eE/r}{c^2} = \frac{W_i+eE/r}{c^2}. \qquad \text{(x)}$$

We may further choose our origins of time, in the presence and absence of the field respectively, such that

$$r_0 = r_{0,i}. \qquad \text{(xi)}$$

So that we finally see from (vii), (viii), (x) and (xi) that the set of equations (viii) which define the complete motion along $\Sigma_{i,s}$, would also define the motion along Σ_s if we wrote χ for ψ, where

$$\chi = \psi-\omega t'+(\Delta_i-\Delta). \qquad \text{(xii)}$$

In other words, the motion along Σ_s is obtained from the motion along $\Sigma_{i,s}$ by the mere superposition of an angular velocity about Oz equal to

$$\dot{\psi}-\dot{\chi} = \omega\, dt'/dt = \omega\sqrt{(1-\beta^2)}. \qquad \text{(xiii)}$$

This, of course, is merely a statement of Schott's theorem referred to in the text. We have here established it *as a necessary result of the extended quantum restrictions*, and without considering the period of establishment of the field.